

SEMI-ANNUAL PROGRESS REPORT

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# Rensselaer Polytechnic Institute

## Semi-Annual Progress Report National Aeronautics and Space Administration Grant NsG-100-60 September 1, 1965 to February 28, 1966

### INTRODUCTION

This tenth semi-annual report from the Interdisciplinary Materials Research program at Rensselaer follows the format established by previous reports. It contains a brief description of the studies that were carried out under each research project during the report period along with some interim results and a description of the studies that are planned for the ensuing six months.

Two new investigators, Professor N.S. Stoloff and Professor R.J. Diefendorf, initiated research programs during this report period. They are, in general, pursuing studies in the areas that had been under investigation by Professor W.R. Clough and Professor R.C. DeVries respectively.

### RESEARCH PROJECTS

#### Mechanical Properties of Polymers

470.05

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#### A. Fracture of Polymers

Fracture data on polymethylmethacrylate under compound loading history, viz. sinusoidal stress superposed upon a creep load, have been obtained and are being analyzed with the use of a theory of fracture for viscoelastic, glasslike polymers. The data indicate a cyclical relationship between applied mean load and the service time (e.g., time to failure). Because of the complexity of the theoretical

relationships for compound loading failure, analog solutions to the differential equations involved are now being considered. Theoretical analysis of the stress field in the vicinity of a flaw within a viscoelastic-plastic material is continuing. (Partially supported by the Institute of Paper Chemistry).

#### B. Polymer Network Mechanics

Application of minimum free energy criteria to the formulation of constitutive equations for highly elastomeric materials is now in progress. The appropriate network equations for a three dimensional body have now been formulated, and solved for the initial moduli of elasticity (at vanishing strain). Solutions for higher order deformations are now in progress. (Supported by the National Science Foundation).

Theoretical and experimental investigations of the domain structure, state of aggregation, and stress field perturbations within composite polymer systems are now being initiated. Specifically, the system glasslike matrix and rubber dispersed phase is now under investigation.

#### C. Viscoelastic Properties of Polymers

Detailed swelling and absorption data on various polymers in solvents of varying cohesive energy density have been obtained and are now being analyzed. These data will be summarized in the next progress report. The apparatus, described previously, used in this study has been found capable of detecting swelling changes smaller than 0.1% of sample volume. The dielectric and dynamic mechanical spectra studies are continuing and data on several systems will be reported in the next progress report.

#### D. High Pressure Studies

Equipment is now being designed to study the high pressure x-ray diffractions of several polymers previously studied by high pressure infrared spectroscopy.

#### A Study of the Interaction of Dislocation with the Discrete Second-Phase Particles in Dispersion-Strengthened Alloys

470.09

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The objective of this program has been to delineate the effects associated with the presence of a distributed second-phase in a crystalline matrix by both theoretical considerations and experimental observations.

During this period, research efforts have centered principally upon experimental observations utilizing both replication and thin film transmission electron microscopy techniques. The specific areas investigated include:

A. Recovery and Recrystallization Kinetics in Two-Phase Systems

It has been well established that the presence of a distributed second-phase inhibits grain boundary migration, particularly secondary recrystallization in dispersion-strengthened alloy systems. Unfortunately, however, the mechanism by which this retardation occurs has never been delineated. Utilizing hot stage transmission electron microscopy and cine<sup>1</sup> sequence recording techniques, studies of the rate of substructural recovery of cold worked structures and the interaction of migrating grain boundaries with second-phase particles have been made. The alloy system investigated is the Al-Al<sub>2</sub>O<sub>3</sub> SAP-type alloy. This alloy has afforded direct observation of these kinetic processes without the concomitant change in distributed phase structure which usually accompanies these high temperature processes. In particular, the thermal effect on the cold worked structures can be described in terms of two distinctive mechanisms. At approximately 0.5 of the absolute melting temperature localized shifting of the individual dislocation boundaries in the cell walls produce changes in relative cell-to-cell misorientation. At higher temperatures, cell wall migration and resultant growth occurs. This work has been completed and formed part of the doctoral dissertation of N. Ramchandran. The results of this investigation are now being written as a paper for publication. In order to determine the generality of this recovery and recrystallization mechanism, studies of this behavior in high purity aluminum are being initiated.

B. Oxidation of Oxide Containing Alloys

The use of hot stage electron microscopy affords the opportunity to study in situ, the oxidation behavior of metal alloys. In particular, the influence of a distributed oxide phase on the subsequent nucleation and growth of oxide films can be followed in detail. Thin film specimens of Al-Al<sub>2</sub>O<sub>3</sub> SAP-type alloys have been oxidized in the electron microscope at partial pressures of oxygen

of approximately  $10^{-5}$  torr in the temperature range of from 300 to 600° C. The oxide growth on the aluminum matrix at lower temperatures occurs rather slowly. The interface is impeded by the presence of second phase  $Al_2O_3$  particles where such particles extend through the foil surface. This impeding effect is probably due to beam and column contamination around these surface particles acting as a mechanical barrier to oxygen. Electron diffraction studies of the oxide structure indicate that the aluminum oxide formed at the lower temperature is of a type not previously reported. At higher temperatures, within the previously formed oxide film, a higher crystalline form of aluminum oxide nucleates and grows. This oxide is probably  $Al_2O_3$ , the same oxide phase intentionally present in the alloy. It has been noted that the  $Al_2O_3$  in the SAP alloy can, but need not, act as the nucleation site for this oxide formation. Interestingly, this oxide formation is reversible in the microscope indicating that these observations are being made under close to equilibrium conditions. This program has been completed and formed part of the doctoral dissertation of N. Ramchandran. A paper covering this study has been submitted for publication.

#### C. Work Hardening Behavior in Precipitation-Hardened Alloys

The role of the interface structure upon dislocation distributed phase interactions, appears upon the basis of theoretical considerations, to be of prime importance in the development of substructure during deformation. The substructural development in an Al- $Ag$  precipitation-hardened alloy has been followed by means of transmission electron microscopy.

In this alloy, studies of the two phase structure have centered upon aging treatments which produce the  $\gamma'$  precipitate. This phase forms as platelets within the alloy matrix dividing the structure into blocks. Deformation in this system produces three stages of substructure development. Initially, the precipitate-matrix interfaces act as dislocation sources and sink so as to provide no increase of substructure. Instead, each precipitate-bounded matrix block deforms rather uniformly as an entity producing block to block misorientations. This can be followed rather neatly by moiré fringing appearing as a result of matrix to precipitate plate rotations, in effect, a type of microstrain gage. In this deformation range no increase in flow stress for the alloy occurs. At higher deformations, dislocation motion is no longer contained within a matrix block, and particle shear coupled with increases in substructure occurs. As soon as this substructural change happens, the flow stress of the alloy increases by approximately 50%. At very high deformations, dynamic recovery occurs, evidenced by symmetric tangle formation. This work has been completed and has been accepted for publication in Acta Metallurgica. This material was incorporated in the doctoral dissertation of C. Barton.

#### D. Fracture Behavior

The influence of a distributed phase upon fracture mode and crack propagation is being studied in steel. Replication studies of the fracture surfaces of these alloys broken in fatigue, are being used

to establish the mechanism by which dissolved gasses, particularly hydrogen, affect fatigue fracture. This program is currently in progress and is being handled in cooperation with Dr. H. Rogers of the G. E. Research Laboratory.

#### E. Precipitation Kinetics

The formation of quench and solute induced defect formation apparently control the nucleation and growth kinetics of many precipitate phases. In the studies of the Al-Ag system, several observations were made of such nucleation behavior. Currently, this area is being pursued with the emphasis on the formation of the defect structure and its role upon the nucleation and growth mechanisms involved in the formation of the  $\chi_1$  phase.

#### F. Martensite Transformation

The kinetics of the martensite transformation in the Fe-C system have proved elusive. As a result of recent work in this laboratory, it is felt that this transformation may be controlled by the shear strength of austenite. For this reason an investigation of the kinetics of the martensite transformation as a function of austenite strength has been undertaken. This program is currently in progress. In addition, the effect of quench rate upon the Ms transformation temperature in a series of five different steels are being determined.

#### G. Theoretical Studies

Theoretical studies of dispersion-strengthening based upon dislocation theory are progressing on a continuing basis. A review article on the mechanisms proposed for dispersion-strengthening has been written and will be presented in June at the conference, "Oxide Dispersion-Strengthening." This paper will be published in the proceedings of the conference.

During this period, C.J. Barton and N. Ramchandran completed their studies and were awarded the Ph.D. degree.

#### Mechanisms of Solidification

470.10

Senior Investigator:	W.J. Childs, Ph.D. Professor of Metallurgical Engineering
Research Staff:	J.J. Frawley, M. Met. E. Graduate Assistant

The investigation of the effects of vibrational energy on the nucleation and growth of supercooled metals and alloys was continued. In the last report it was noted that the ultrasonic vibration of pure bismuth caused nucleation when cavitation occurred. However, it has now been observed that the sound field did not refine the

grains and the resulting grain size was the same as specimens statically supercooled the same amount. In the case of pure tin, vibrated specimens showed grain refinement. This grain refinement in tin was due to fragmentation of the long thin cylindrically shaped dendrites causing new nucleation centers. The bismuth dendrites, at this degree of supercooling are larger and coarser, and are not easily fragmented by the vibrations.

With the addition of 10% tin to the bismuth, the growth habit of the dendrites was changed, giving a finer structure. The application of ultrasonic energy to this alloy as it solidified greatly reduced the grain size and reduced gross segregation.

The growth direction of bismuth-10% tin alloy was determined. The alloy was supercooled approximately 13 C° and nucleated by a seed crystal. After recalescence occurred, the remaining liquid was removed by the vacuum decanting technique. The growth direction was determined by x-ray diffraction as the  $\langle 111 \rangle$  direction, the same as for pure bismuth, but the growth habit was different due to the presence of the tin.

#### Ultrasonic Research

470.11

Senior Investigator:	H.B. Huntington, Ph.D. Professor of Physics
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The project is concerned with using pulsed ultrasonics to investigate elastic properties of solids.

Present work consists of two projects; the first attempts to achieve beam mixing, or the mixing of two ultrasonic beams to generate a third, and the second attempts the measurement of the elastic constants of inorganic crystals. In the first project we have been using two high power Arenberg transmitters at 5 Mcs and 15 Mcs to generate a 20 Mcs signal but the technique is still under development. In the second project we are looking at anthracene crystals as commercially supplied, and also specimens of higher purity as provided by workers interested in better characterized material.

The plan for the beam-mixing work is to proceed from studies in isotropic media to work on single crystals. Ultimately we hope to use the technique to make semiquantitative measurements of third order elastic constants.

Ultrasonic Pulse Interferometry

470.12

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During the past six months attention has been focused on the remarkable behavior of AgI and other metal halides confined in a radial pressure gradient by a pressure cell which utilizes two diamond anvils and permits visual microscopic examination at high pressure. In the case of AgI above about 5 kb and under the influence of the radial pressure gradient imposed upon the specimen by the pressure cell geometry,  $I_2$  is observed to migrate toward the central high pressure region, while Ag is observed in the low pressure, peripheral areas. Experiments with specimens doped with  $I_2$  and at different temperatures, as well as calculations using different diffusion models, suggest that grain boundary diffusion is the dominant effect, the more compressible component,  $I_2$ , diffusing towards the central high pressure region. The calculations and detailed photographic studies are being prepared for publication.

Ultrasonic studies are continuing of the metals, Al, Bi, Co, Cu, Fe, Mg, Ni, and of several silicates. The pressure dependence of the density and elastic constants are being measured to over 50 kb. Various corrections for the elastic and crushing properties of the gasketing materials have proved quite troublesome but are now reasonably well determined. The modifications of the pressure cell required for introducing temperature as a variable have been nearly completed.

The Relation of Molecular Structure and Intermolecular 470.15  
Action in Flow of Polymers and Polymer Dispersions  
as a Function of Temperature and Shear Rate

Senior Investigator: W.H. Bauer, Ph.D.  
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The objective of the research has been to study the relation between flow properties of liquid polymers such as the low molecular weight polybutadienes and the molecular structure and distribution of the polymeric systems.

The flow behavior of some low molecular weight polymers was studied as a function of shear rate, shear stress and temperature. The polymers

included polybutadienes, random carboxyl and carboxyl terminated polybutadienes, carboxyl terminated butadiene-acrylonitrile and acrylonitrile-butadiene copolymers.

Measurements were made in the temperature range 3.8 to 73° C. A cone and plate viscometer and pressure capillary viscometer were used to cover the shear rate range 1 to  $10^5 \text{ sec}^{-1}$ . Measurements were carried out with various capillary radius to length ratios.  $\bar{M}_w$   $\bar{M}_n$  values were calculated from molecular weight distribution data obtained by Gel Permeation chromatography. Limiting viscosity numbers were also determined.

In the range of shear rates studied, all polymers showed a limiting viscosity at low rates of shear and a region of shear rate thinning. The log viscosity-log shear rate flow curves for each sample at the various temperatures were superimposable by linear shifts. Energies of activation calculated according to the method of Fox and Loshaek were found to have values characteristic of the molecular structure. Normal stresses developed in capillary flow as measured by entrance effects showed some dependence on structure. Flow results were compared with the Bueche-Harding experimental standard curve and the Bueche theoretical curve.

The presence of polar groups in the polymer chain increased the energy of activation and the relative magnitude of the viscosity. The log viscosity-log shear rate flow curves for all the samples at any constant temperature were superimposable by linear shifts in two distinct classes according to differences in molecular weight distribution.

In future work it is planned to extend the study to a greater range of molecular weights and chemical structures.

#### The Influence of Deformation Mode on the Ductile to Brittle Transition of FeCo-V Alloys 470.18

Senior Investigator: N.S. Stoloff, Ph.D.  
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Research Staff: K.R. Jordan, M.S.  
Research Assistant

#### A. Fracture of Fe-Co-V Alloys

The objective of this program is to determine the role of Cross-Slip on Brittle Fracture. During this report period, the material (Fe-49 Co-2V) required in this program has been procured and fabricated to wire. A tensile test apparatus has been fabricated with efforts to insure axial alignment of the wire grips.

Suitable working and annealing schedules have been determined and control of grain size (a primary test variable) has been demonstrated over the range  $7 \times 10^{-4} \text{ cm.}$  to  $1 \times 10^{-2} \text{ cm.}$

Preliminary tensile tests verify the expected dependence of yield and fracture stress on grain size, however, repeated failures have occurred in the wire grips during tensile tests of ordered material.

Modification of the wire grips is required to preclude failures in the grips. It is anticipated that specimen preparation and tensile testing will be concluded during this period and electron transmission microscopy will be initiated to establish the relationship between fracture behavior and microscopic deformation modes.

#### B. Transient Creep of Alloys

The objective of this program is to determine the rate-controlling mechanisms operating during the low temperature, thermally activated deformation of BCC and FCC-solid solutions. Emphasis is being placed on BCC solid solutions because the results should aid in revealing the controversial mechanism controlling the thermally activated deformation of pure BCC metals.

During this report period, activation volumes and activation energies have been determined over a range of temperatures extending from -196 to 200 degrees Centigrade as a function of stress and strain for a series of five compositions in the Cb-Ta system extending from 28.03 to 90.68 weight per cent Ta. Tests are being performed on a constant stress creep machine which has been slightly modified in order to facilitate the testing procedure.

Three alloys in the Cb-V alloy system consisting of 5, 10 and 15 per cent V have been drawn down to wire specimens and recrystallized. Also, Ni-Pt and Ni-Pd alloys have also been drawn down to wire and are presently undergoing recrystallization studies.

Activation energies and activation volumes will be determined for the Cb-V, Ni-Pt, and Ni-Pd alloys, as will additional activation energies for the Cb-Ta alloys.

The athermal component of the flow stress will be experimentally determined to find how the activation energy and activation volume vary with the effective stress (applied stress minus the athermal stress).

#### Low Temperature Physics

470.19

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This investigation into properties of low melting superconductors continues to be concentrated in two areas.

#### A. Ultrasonic Attenuation in Superconductors

In order to interpret results of ultrasonic attenuation measurements it has become necessary to thoroughly understand an amplitude dependent effect mentioned in the previous report. This requires careful measurements at the smallest possible signal levels which we are now in the process of making. Further experiments involving  $\gamma$ -irradiation, plastic deformation, and alloying are in progress to definitely identify the proposed dislocation source of the amplitude effect. We have also observed this effect in thallium and mercury crystals, where energy gap measurements (the main goal of this work) are getting underway.

#### B. Superconductivity and Lattice Defects

The previous report discussed a calculation of the increase of current carrying capacity of a superconductor brought on by the introduction of lattice defects. The prediction regarding temperature dependence of this increase has been verified in experiments while the magnetic field dependence appears to be incompletely explained. Further work is in progress to improve both the theoretical and experimental position of this work. Ultrasonic attenuation has been put to work in studies of defects in the materials of interest and seems to hold considerable promise.

### Pyrolytic Materials

470.20

Senior Investigator:	R.J. Diefendorf, Ph.D. Associate Professor of Metallurgical Engineering
Research Staff:	B. Butler, B.S. Graduate Assistant A. Kinawi, M.Sc. Graduate Assistant

One of the major aims of materials engineering is to determine the relationship of forming processes to structure to properties of materials. The research funded in this project has been performed to determine these relationships for several materials which are critical to aerospace applications.

During the past six months, two vacuum furnaces and associated equipment have been assembled for vapor deposition studies. Two major areas of effort are planned for the future:

## 1. High Temperature Electronic Materials

Graphite and boron nitride have nearly identical crystal structures and lattice constants. Graphite has a small band gap and is essentially metallic in behavior, while boron nitride is one of the best insulators known. Conventional processing techniques have not been able to form ternaries, since at the necessarily high process temperatures, boron carbide, the thermodynamically stable phase, is formed. However, vapor deposition can form such ternaries metastably. It is planned to make these compositions and to study the resulting electronic properties.

## 2. Effect of Catalysis on Pyrolytic Graphite

The relationship of deposition conditions to structure and properties is rather well understood for deposition of pyrolytic graphite from methane. It is also known that boron trichloride can strikingly alter the deposition rates and structure of pyrolytic graphite. We plan to study the reasons for this catalysis.

### Dispersion-Strengthened Materials

470.23

Senior Investigator:	F.V. Lenel, Ph.D. Professor of Metallurgical Engineering
Research Staff:	G. Leverant, B.S. Research Fellow H. Nayar, M.S. Graduate Assistant

Dr. Hirschhorn's work on the properties and structure of internally oxidized silver-magnesium and silver-aluminum alloys has been written up as a paper and submitted to Transactions Quarterly of the American Society for Metals.

Dr. Leverant completed his work on the creep properties of dispersion strengthened silver-magnesium alloys and submitted the results as a Ph.D. thesis which has been accepted by the department. It is intended to write papers covering both the work of Dr. Leverant in his Ph.D. thesis and of Mr. Singh in his Master's thesis (see Semi Annual Progress Report of September 1965) and submit these papers for publication.

Mr. Nayar completed his experimental work on ice strengthened by a fine dispersion of silica. He is now developing a theory to explain the strengthening observed in his experiments. He will submit a Ph.D. thesis comprising both experimental work and theory.

Work is under way on the structure, the mechanical and the corrosion properties of lead strengthened by a fine dispersion of lead oxide.

Metallic Dissolution

470.25

Senior Investigator: N.D. Greene, Ph.D.  
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The purpose of this program is to determine the basic corrosion and electrochemical characteristics of iron and iron alloys (steels).

Multiple correlation analysis of corrosion test data has been employed to determine relationships between corrosion behavior and chemical composition. Phosphorus, carbon, and high manganese have a detrimental effect on the corrosion rate, while small additions of copper are beneficial.

Similar analyses will be applied to electrochemical data obtained from anodic and cathodic polarization experiments.

Nuclear Magnetic Resonance Research

470.26

Senior Investigator: P.A. Casabella, Ph.D.  
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The primary purpose of this investigation is to study the effects of elastic strain on the nuclear electric quadrupole interaction in sodium chloride and sodium bromide. These effects are best described by a tensor of fourth rank,  $S$ , connecting the field gradients with the elastic strains. With the exception of the sodium ion in NaCl, this is the first experimental determination of the  $S$  tensor for these ions by the application of static elastic strain. Knowledge of the  $S$  tensor is particularly important for use in resolving the conflict between experimental and theoretical values of the ionic antishielding factors  $(1 + \gamma)$ .

Oriented single crystals of these alkali halides were strained. This lowered the symmetry of the lattice and produced electric field gradients at the nuclear sites. These gradients cause a perturbation of the NMR spectra by interacting with the electric quadrupole moment of the nucleus. In the case of a  $[111]$  stress in NaCl, the  $\text{Cl}^{35}$  first order satellites were directly observable as extra bumps outside the main resonance. The field gradients were determined from the changes under strain of the recorded spectra. The field gradients were then used to find the  $S$  tensor components which are shown in the following table:

Electric Field Gradient-Elastic Strain Tensor Components

Nucleus	Crystal	$S_{11}$ cgs-esu	$S_{44}$ cgs-esu
$\text{Na}^{23}$	NaCl	$2.60 \times 10^{15}$ $\pm 15\%$	$1.09 \times 10^{15}$ $\pm 10\%$
$\text{Na}^{23}$	NaBr	2.44 $\pm 30\%$	0.824 $\pm 20\%$
$\text{Cl}^{35}$	NaCl	3.29 $\pm 20\%$	4.02 $\pm 5\%$
$\text{Br}^{79}$	NaBr	Not Observed	6.73 $\pm 30\%$

The ratio of the measured field gradient to the gradient produced by a similarly strained lattice of point ions in the effective antishielding factor ( $\beta$ ) for the ions under study. These effective antishielding factors are shown in the next table along with the available theoretical antishielding factors ( $1+\gamma$ ).

Effective Antishielding Factors ( $\beta$ )

Nucleus	Crystal	$\beta_{11}$	$\beta_{\eta 4}$	Theoretical ( $1+\gamma$ )
$\text{Na}^{23}$	NaCl	10.36	8.68	5.1-5.5
$\text{Na}^{23}$	NaBr	11.56	7.82	5.1-5.5
$\text{Cl}^{35}$	NaCl	13.11	32.02	28,50,57, 86-88
$\text{Br}^{79}$	NaBr	-	63.8	100, 124

The discrepancies between the corresponding  $\beta$  and  $1+\gamma$  values are explained by a consideration of nearest neighbor overlap effects for the sodium ions and first and second nearest neighbors overlaps for the halogens. The point ion plus overlap model provided good agreement with the observed effective antishielding values. In addition, the formalism for pure covalent charge transfer effects was developed. However, covalency was not believed to be very important and was not required in order to explain the results of these experiments.

X-Ray Scattering

470.28

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Studies of the crystal and molecular structure of the coordination compounds of the platinum group metals and the lattice dynamic studies of certain metals and alloys are being continued.

The X-Ray Laboratory has been engaged in an extensive program of instrumentation involving the automation of a full circle diffractometer. This will permit the acquisition of more detailed and precise diffraction data resulting in more significant crystal and molecular structure analyses. To this end, a DEC PDP-8 digital computer has recently been acquired for the purpose of providing real time control of the automated diffractometer.

The liquid helium cryostat for X-Ray studies has been delivered and adapted for use with existing equipment. The first material being studied with this system is zinc. In conjunction with these experimental studies are theoretical calculations of the thermal diffuse x-ray scattering corrections which must be made. One such method has been accepted for presentation at the Seventh International Congress and Symposium of the International Union of Crystallography.

#### Thermal Properties of Polymers

470.29

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#### A. Thermal Conductivity

Measurements of the thermal conductivity anisotropy in oriented polymethylmethacrylate are being completed. These measurements have been made on specimens oriented by hot drawing to relative elongations of 200%, 400%, and 600%. As expected the polymer shows increased thermal conductivity in the direction of orientation, which increases with the degree of orientation. Further data will be taken on polystyrene and polyvinyl chloride to provide a set for comparison with theoretical predictions reported earlier.

## B. Structure

The studies of polymer structure by electron microscopy of microtomed sections are proceeding along two lines.

Polyethyleneterephthalate specimens are being prepared under conditions that permit monitoring the crystallization rates. Observations on these specimens will provide direct comparisons between three dimensional structure and crystallization kinetics.

Nylon - 66 specimens are being prepared by controlled isothermal crystallization followed by cold drawing. Observations on these samples are yielding direct data on structural changes, particularly with respect to crystal deformation, that accompany cold-drawing of crystalline polymers.

### Glass and Non-Metallic Materials 470.30

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The objectives of this work are twofold: (a) to correlate structures and properties of glasses and other non-metallic solids, and (b) to prepare new non-metallic materials and study their properties.

During this period, research has been carried out on (1) semi-conducting glasses, (2) ceramic-metal interfaces, (3) glass-crystal composite materials and (4) vapor deposition of nitrides. These projects are being continued.

### Vibrational Spectroscopy Inorganic Substances 470.31 in the Vapor Phase

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Research Staff: G. Kelly, B.A.  
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The attempts to obtain infrared spectra of  $\text{NaNO}_3$ ,  $\text{KNO}_3$ , and  $\text{KNO}_2$  were continued during the period covered by this report. As previously noted extensive decomposition of the nitrates occurs. Bands characteristic of nitrite ion,  $\text{NO}$ , and  $\text{NO}_2$  are obtained over the temperature range from  $450^\circ\text{C}$  to  $650^\circ\text{C}$ . The problem of deposition of solid material on the cell windows has not been resolved. To study the decomposition further, a cell containing a heated platinum 80 mesh screen has been constructed. With this cell it has been possible to obtain the spectra of molten  $\text{NaNO}_3$ ,  $\text{KNO}_3$ , and  $\text{AgNO}_3$ . The spectrum of  $\text{AgNO}_3$  shows broad unresolved absorption peaks, but it has not been possible to identify positively decomposition products. This aspect of the work is continuing, and attempts to study the time dependence of the melt spectra will be undertaken.

Irreversible Thermodynamics of the Solid  
State of Linear High Polymers

470.32

Senior Investigator: B. Wunderlich, Ph.D.  
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Research Staff: S. Wolpert  
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The measurements of the time dependent specific heat of glasses in the transition range are being continued, and the poly (methyl methacrylate) data are almost completed. Glucose and selenium are the next two substances to be studied. The purpose of this research is to collect data on 5 to 10 glasses over the next two years, so that a previously developed theory can be applied to a broad range of different glasses. Possible extensions of the theory will be developed.

The study of the seeding of metastable polyethylene melts with extended chain equilibrium crystals has been concluded. Out of this research grew an investigation of the crystallization mechanism of polymer crystals which lead to an entirely new picture of growth of folded chain crystals. This new research will also come to a conclusion within the next month.

An investigation into the equilibrium thermodynamics of polymers and copolymers using calorimetric and dilatometric techniques will start in March. For this project, Dr. Hamada from Kyoto University in Japan, will join our group and spend 1 year as a post doctoral fellow with the project.

Ultra-Low Temperature Solid State Physics Research

470.33

Senior Investigator: G.L. Salinger, Ph.D.  
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Graduate Assistant

The object of the program is to measure thermal properties of magnetic salts at low temperatures. In particular, thermal conductivity will be measured in order to determine the interactions in the magnetic and lattice systems.

In the past six months, the construction of the cryostat has continued with the completion and testing of most of the components. This phase should be completed shortly and the experimental program initiated.

Thermal Decomposition of Inorganic 470.34  
Coordination Compounds

Senior Investigator: R.A. Bailey, Ph.D.  
Assistant Professor of Inorganic  
Chemistry

Research Staff: I.R. Feins, B.S.  
Graduate Assistant  
F. Montillo, M.S.  
Graduate Assistant

The objectives of this work are to determine the manner in which metal complexes of organic ligands decompose thermally, and so gain information on the stabilities and reaction of such compounds.

Complexes of urea and substituted ureas were chosen for initial study, as they provide a series of ligands with related, and not too complicated, structures. It became apparent that further work was needed to characterize the compounds formed before the thermal decomposition reactions could be interpreted properly. A number of new complexes of this sort have been prepared and their structures determined from infrared and ligand field spectroscopy, magnetic susceptibility, and other methods. Decomposition studies have been made on zinc, cadmium, mercury, and some transition metal chloride complexes of urea and N-methyl ureas. The reaction proceeds through the rupture of a C-N bond in the ligand, giving ammonia (methylamines in the case of the N-substituted ligands) as well as other volatile products which are being investigated by infrared and mass spectroscopy. Final residual products are usually the metal chloride, although in certain cases, oxides may form. Intermediate complexes resulting from partial loss of ligand have been found and are being investigated further.

Thermodynamics and Kinetics Vaporization 470.35  
Processes for Inorganic Materials

Senior Investigator: H. Wiedemeier, Ph.D.  
Assistant Professor of Chemistry

## Research Staff:

W.J. Goyette, B.S.  
Graduate Assistant  
A. Khan, B.S.  
Graduate Assistant  
A.G. Sigai, B.S.  
Graduate Assistant

Within the framework of thermodynamic and kinetic studies of transition metal -Group VI compounds, emphasis has been placed during the past six months' period upon the study of some of the solid state properties of these materials.

Growth conditions and habit of single crystals as a function of various experimental parameters were investigated in the case of sulfides and selenides. We succeeded in the synthesis of high purity single crystals of manganese sulfide of large area and extremely low thickness. Such specimens are perfectly suitable for electro-optical studies, which are presently in progress.

In the case of selenides we obtained large-sized single crystals of tetrahedral and octahedral form with well developed faces. These samples will be used for Knudsen and Langmuir studies.

In connection with the investigation of the ternary Mn-Cd-S system we observed that the growth conditions are affected by the pressure previously exerted upon the material. Possible effects on structural properties are presently being studied.

A vacuum-thermo-balance and a high-temperature furnace will be set up in the immediate future for vaporization studies of the above-mentioned materials.

Spectroscopic Studies of Synthetic Reversible 470.36  
Oxygen-Carrying Chelates

## Senior Investigator:

S.E. Wiberley, Ph.D.  
Professor of Chemistry

## Research Staff:

T. Comfort, M.S.  
Graduate Assistant

Additional experiments to prepare iron (II) bis dimethylglyoxime as a solid have been unsuccessful. Although the complexes  $\text{Fe}(\text{DM})_2 \cdot 2\text{NH}_3$  and  $\text{Fe}(\text{DM})_2 \cdot 2\text{Pyridine}$  have been prepared, efforts to remove the base molecules result in decomposition but without the formation of  $\text{Fe}(\text{DM})_2$ . Solution experiments further indicate that the  $\text{Fe}(\text{DM})_2$ , if formed, would not be a reversible oxygen--carrying chelate. This project is being phased out.

Electron Spin Resonance

470.37

Senior Investigator: A.C. Greene, Ph.D.  
Assistant Professor of Physics

Research Staff: D.D. Moyle, B.S.  
Graduate Assistant  
D.B. Williams, B.S.  
Graduate Assistant

A series of ionic crystals has been grown for the purpose of studying irradiation effects, particularly atomic displacement processes, due to ionizing radiation. In addition, an electron spin resonance examination of ferroelectric properties, such as phase transitions and domain character, has been started.

Considerable emphasis has been placed upon the design and construction of high performance sample structures. These include resonant cavities of various geometries and also slow wave helical devices. It is particularly important to attain a high steady electric field across sample specimens with the least disturbance of ideal microwave characteristics required for sensitive resonance detection. A double resonance (ENDOR) system has been designed and is nearing completion.

Polymer Characterization

470.38

Senior Investigator: F.W. Billmeyer, Jr., Ph.D.  
Professor of Analytical Chemistry

Research Staff: N.K. Blackwood, B.S.  
Graduate Assistant  
E.C. Rhodes,  
Graduate Assistant

A photometer has been designed for the precise calibration of photometric standards by the method of addition of light fluxes. Preliminary experiments are in progress, and construction awaits the delivery of components on order.

The precision and accuracy in color measurement of eight commercial colorimeters and spectrophotometers was studied. Extensive measurements were made, mostly on equipment loaned to the Color Measurement Laboratory, using a wide variety of industrially-important samples. Computer programs were written to analyze the data. Publications are in preparation.

TECHNICAL PAPERS SUBMITTED FOR PUBLICATION

Wilson, R.H., Skelton, F., Katz, J.L.

"Measurements of X-Ray Debye Temperature of Pure Nickel and Chromium at Thermal Temperatures Ranging from 100° to 500° K"  
Submitted to Journal of Physical Chemistry of Solids

Cessna, L.C., Jr., Sternstein, S.S.

"The Fracture Strengths of Glassy Polymers"  
Submitted to the Journal of Polymer Science

Wunderlich, B., Cormier, C.M.

"Seeding of Supercooled Polyethylene with Extended Chain Crystals"  
Submitted to Journal of Physical Chemistry

Secrist, D.R., Mackenzie, J.D.

"Glow Discharge Deposition of Oxide Films at Low Temperatures"  
Published in Journal of Ceramics Society

Cooke, F.W., Bradt, R.C., DeVries, R.C., Ansell, G.S.

"Dielectric Aging and Microstructure in the System  $\text{BaTiO}_3\text{-CaTiO}_3$ "  
Submitted to Acta Metallurgica

Hingorany, A.R., Lenel, F.V.

"Properties of Internally Oxidized Columbia-Zirconium Alloy"  
Submitted to ASM Transactions Quarterly

Natesh, R., Ansell, G.S.

"Oxide Growth in a  $\text{Al-Al}_2\text{O}_3$  SAP-Type Alloy by Hot Stage Transmission Electron Microscopy"  
Submitted to Acta Metallurgica

Secrist, D.R., Mackenzie, J.D.

"Deposition of Silica Films by the Glow Discharge Technique"  
Submitted to Journal of Electro Chemical Society

Hirschhorn, J.S., Lenel, F.V.

"Observations on Internally Oxidized Silver-Magnesium and Silver-Aluminum Alloys"  
Submitted to ASM Transactions Quarterly

DeVries, R.C., Jogle, D.B.

"Section II - Structure Property Relationships in Itacolumite"  
Submitted to "Science"

Shaw, R.W., Mackey, W.F., Woo, D.S., Welsh, W., Dionne, G.

"Annealing of Dislocation Pinning Centers in the Temperature Range 120° K to 180° K in Alkali Halide Crystals"  
Submitted to Journal of Applied Physics

Collins, E.A., Bauer, W.H.

"Analysis of Flow Properties in Relation to Molecular Parameters for Polymer Melts"  
Published in the Transactions of the Society of Rheology

## APPENDIX A

### Members of Interdisciplinary Materials Research Center Faculty Committee

S.E. Wiberley, Chairman	Professor of Analytical Chemistry and Dean of the Graduate School
G.S. Ansell	Professor of Metallurgical Engineering
W.H. Bauer	Professor of Physical Chemistry and Dean of the School of Science
A.A. Burr	Professor of Metallurgical Engineering and Dean of the School of Engineering
E.F. Nippes	Director of the Research Division
H.B. Huntington	Professor of Physics, Chairman of the Department of Physics
G.J. Janz	Professor of Physical Chemistry, Chairman of the Department of Chemistry
F.V. Lenel	Professor of Metallurgical Engineering, Chairman of the Department of Materials
S.S. Sternstein	Associate Professor of Chemical Engineering
J.M. LoGiudice	Administrative Director of the Interdisciplinary Materials Research Center